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(54) Title: CATIONICALLY MODIFIED POLYSACCHARIDES

(57) Abstract: A modified polysaccharide having enhanced surface charge. The polysaccharide is modified to include a cationic polymer, preferably a polyquaternary amine, and has a surface charge from about +5 to about +20 mV. The modified polysaccharide can be advantageous incorporated into a papermaking furnish with enhanced retention.

CATIONICALLY MODIFIED POLYSACCHARIDES

Field of the Invention

5 The present invention relates to modified polysaccharide as a filler and strengthening aid for paper and board products and, more particularly, to modified polysaccharide having enhanced surface charge.

Background of the Invention

10 One goal in papermaking is to increase the amount of filler in the ultimate product so as to reduce the amount of fiber, a relatively expensive component. Increasing the amount of filler must not have an adverse effect on the paper's sizing and other necessary properties. Among fillers, starch is attractive because of its low cost and availability. In general, unmodified raw starch is not well retained in
15 papermaking furnishes due to the lack of an effective interaction with fibers and retention aids. Despite this disadvantage, methods have been devised that utilize starch as a filler in papermaking.

 In most paper and board manufacturing, starch is fully cooked and used at a size press. Size press starch can include additives that impart desirable properties to a
20 paper or board such as improved printing, stiffness, bond, dusting, surface pick, among others. Cationic starch is typically added at the papermachine wet end and can improve a paper's strength properties and fine particle retention. Other charged synthetic polymers can be combined with cationic starch to improve overall fine particle retention.

25 Raw uncooked and unmodified starch particles are not added to the wet end of a paper machine due to their unacceptably low retention. Raw starch has a particle surface charge near zero when slurried in water. This lack of surface charge results in a weak interaction with charged retention aids and/or fibers. Without strong interaction (e.g., chemical attachment), starch cannot be retained well in a papermaking
30 system. Mechanical filtration of starch particles can result in some starch retention in a fibrous web, but such retention requires a specific type of headbox configuration.

 However, by adding a surface charge to the raw starch particles, it is possible to dramatically increase starch retention in a web. Such increased starch retention is achieved through the use of retention aids that form a bridging attachment between the
35 charged starch particles and fiber surfaces. Adding charge to raw starch has been previously accomplished by chemical modification of starch through the covalent

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attachment of certain functional groups, for example, quaternary amine groups, to the starch. In papermaking, these chemically modified starches are typically fully cooked and then added in the papermachine's wet end. Such a chemical modification process adds considerable cost to the starch and, furthermore, does not result in a starch
5 having sufficient surface charge to improve retention of uncooked starch significantly beyond that of raw unmodified starch.

Accordingly, there exists a need for an economical filler for use in papermaking methods that provides for increased particle retention without adversely impacting sizing. A need also exists for fillers having increased retention and, in addition, impart
10 strength to paper products into which they are incorporated. The present invention seeks to fulfill these needs and provides further related advantages.

Summary of the Invention

In one aspect, the present invention provides a modified polysaccharide having
15 enhanced surface charge. The polysaccharide of the invention is a polysaccharide that has been modified to include a cationic polymer. The modified starch formed in accordance with the present invention has a surface charge from about +5 to about +20 mV. The modified polysaccharide can be advantageous incorporated into a papermaking furnish with enhanced retention.

20 In another aspect of the invention, paper products that include the modified polysaccharide having enhanced surface charge are provided. Paper products that include the modified polysaccharide have increased strength compared to similarly constituted paper products that do not include the modified polysaccharide. In one embodiment, the paper product includes cellulosic fibers and the modified
25 polysaccharide. In another embodiment, in addition to cellulosic fibers and modified polysaccharide, the paper product further includes a retention aid that enhances the retention of the modified polysaccharide to the fibers. The retention aid can be either a positively or a negatively charged retention aid.

In further aspects, the invention provides methods for forming the modified
30 polysaccharide having enhanced surface charge and methods for forming paper products having increased filler retention and increased strength through the incorporation of the modified polysaccharide.

Brief Description of the Drawings

35 The foregoing aspects and many of the attendant advantages of this invention will become more readily appreciated as the same become better understood by

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reference to the following detailed description, when taken in conjunction with the accompanying drawings, wherein:

FIGURE 1 is a schematic illustration of a representative modified polysaccharide formed in accordance with the present invention.

5

Detailed Description of the Preferred Embodiment

In one aspect, the present invention provides polysaccharide having enhanced surface charge. The polysaccharide has been modified to include a cationic additive that imparts a positive charge to the polysaccharide surface. As used herein, the terms "polysaccharide" and "starch" are interchangeable, and the terms "modified starch" and "modified polysaccharide" refer to a polysaccharide having enhanced surface charge formed in accordance with the present invention.

Suitable cationic additives include materials that can be irreversibly and/or strongly associated with starch and, when associated with starch, enhance its surface charge. Cationic additives include cationic organic polyelectrolytes and polymers. Preferably, the cationic additive includes a cationic polymer such as a polyquaternary amine. In a preferred embodiment, the cationic additive is a relatively low molecular weight, highly positively charged polyquaternary amine having a molecular weight in the range from about 1 to 5 million grams per mole and about 3 milliequivalents quaternary amine per gram. Such a polyquaternary amine is commercially available under the designation Nalco 7527 from Nalco Chemical Co., Naperville, IL. The cationic additive is present on the starch in an amount from about 1 to about 15 pounds/ton starch on a dry basis and, preferably, about 5 pounds/ton starch.

Other cationic additives that are useful in forming the modified starches of the invention include cationic polyacrylamides, aluminum sulfate, chitosan, polyamines, polyamidoamines, polyethylenimines, polyamide-epichlorohydrin (PAE), polyalkylene polyamine-epichlorohydrin (PAPAE), and amine polymer-epichlorohydrin (APE).

The modified starch formed in accordance with the present invention has a surface charge in the range from about +1 mV to about +100 mV and, preferably from about +5 to about +20 mV as determined by the zeta potential measurement.

Starches from a variety of sources can be modified to provide starches having enhanced surface charge. Suitable starches are available from corn, potato, tapioca, pea and wheat, among other sources.

The modified starch of the invention can be formed from a slurry of raw uncooked starch and cationic additive in water. In one embodiment, raw uncooked starch is added to pH 10 water to provide a slurry having about 7% solids. The starch

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swells in the alkaline solution which appears as a milky paste. Although swelling occurs, the starch remains in the form of discrete particles. However, at higher pH, the starch can gel as a result of denaturation (i.e., chemical cooking). Gelatinization during modified starch formation is to be avoided. Without being bound by the following theory, it is proposed that the cationic additive diffuses into the surface of the swollen starch particle to provide a surface charged particle. The cationic additive is then entrapped within the starch particle on adjusting the pH of the cationic additive-treated starch slurry to about neutral pH. On addition of the cationic additive, the starch changes in appearance from a milky paste to granular sand-like particles. Alternatively, in another embodiment, the modified starch can be formed by adding to the cationic additive to a starch slurry at about pH 7. Although the amount of swelling at neutral pH is less than that which occurs at alkaline pH, the swelling is sufficient to provide a modified starch having enhanced surface charge. In a preferred embodiment, the modified polysaccharide is a granular polysaccharide.

A schematic illustration of a representative starch particle formed in accordance with the present invention is illustrated in FIGURE 1. Referring to FIGURE 1, modified starch particle 10 includes cationic additives 12 adhered to starch particle 14.

The preparation and properties of representative modified starches having enhanced surface charge are described in Example 1. The measurement of the surface charge of representative surface charged enhanced starch particles formed in accordance with the present invention is described in Example 2.

The modified starch of the invention can be advantageously incorporated into a papermaking furnish. As described below, the modified starch is highly retained by pulp thereby rendering the modified starch an economic filler for paper products. Moreover, the paper products that incorporate the modified starch pulp have improved strength.

The retention of the modified starch in pulp is increased compared to raw uncooked starch. As described in Example 3, Britt Jar experiments demonstrated that the modified starch can be retained by pulp to an equal or greater extent compared to precipitated calcium carbonate (PCC), a conventional filler. Generally, for a fine paper furnish, from about 60 to about 70 percent modified starch was retained under conditions that resulted in the retention of about 45 percent PCC.

The modified starch can be highly retained by pulp to provide a pulp that can yield a paper product having high filler retention. Alternatively, in addition to the modified starch, other retention aids can be added to the pulp to further increase

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modified starch retention. Retention aids include those known in the papermaking art and the anionic and cationic retention aids described below.

An anionic retention aid or additive can be utilized to increase modified starch retention. Anionic retention aids include anionic organic polyelectrolytes and polymers. Preferably, the anionic retention aid includes an anionic polymer such as, for example, anionic polyacrylamide (APAM). In a preferred embodiment, the anionic retention aid is a relatively high molecular weight, slightly negatively charged polyacrylamide. The preferred polyacrylamide has a molecular weight in the range from about 8 to about 15 million grams/mole and is a copolymer of acrylic acid (30 mole percent) and acrylamide (70 mole percent). Such a polyacrylamide is commercially available under the designation Accurac 171 from Cytec Industries Inc., West Patterson, NJ. Alternatively, the anionic polyacrylamide is commercially available under the designation Nugen 24 from Northwest Specialty Chemicals, Vancouver, WA. The anionic retention aid is present in the fibrous pulp in an amount from about 0.1 to about 3.0 pounds/ton fiber and, preferably, about 0.5 pounds/ton fiber.

Other suitable anionic retention aids include high molecular weight anionic flocculants.

As described in Example 3, a representative anionic retention aid (e.g., APAM) is preferably added to the pulp at the wet end of the papermaking machine and can be added to the pulp prior to modified starch addition, simultaneous with modified starch addition, or after modified starch addition. As illustrated in Table 9, the greatest retention (72 percent by weight) was achieved with the addition of the APAM to the pulp followed by the addition of the modified starch. The second greatest retention (58 percent by weight) was the addition of the modified starch to the pulp followed by the APAM addition. Both of these conditions provided a higher filler retention than the typical alkaline fine paper system (45 percent by weight).

Other additives can also advantageously increase the retention of the modified starch by pulp. For example, cationic retention aids and additives can increase pulp retention of the modified starch. Preferably, the cationic retention aid includes a cationic polymer such as, for example, a cationic polyacrylamide (CPAM), which has a relatively high molecular weight and is slightly positively charged. The preferred polyacrylamide has a molecular weight in the range from about 8 to about 15 million grams/mole and is a copolymer of acrylamide (90 mole percent) and a quaternary amine monomer (10 mole percent). Such a polyacrylamide is commercially available under the designation Accurac 182RS from Cytec Industries Inc., West Patterson, NJ.

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The cationic retention aid is present in the fibrous pulp in an amount from about 0.1 to about 12 pounds/ton fiber and, preferably, from about 0.4 to about 6 pounds/ton fiber. Combinations of anionic and cationic retention aids can be used with the modified starch to increase pulp retention.

- 5 Other suitable cationic retention aids include high molecular weight cationic flocculants such as, for example, cationic polyacrylamides commercially available from Nalco Chemical Co., Naperville, IL under the designations Nalco 7530 and 7520.

- Pulps containing the highly retained modified starches can be formed into paper products characterized by having advantageously high filler retention and increased
10 strength. Paper products that benefit from the advantageous incorporation of the modified starch include fine paper, newsprint, bleached board, liner board, medium board, and old corrugated cardboard (OCC), among others.

- Paper products containing modified starch and, optionally, one or more of the retention aids described above can be formed by adding the modified starch and, if
15 desired, the retention aid(s), to a pulp furnish at the wet end of a papermaking machine. Depending on the desired properties of the paper product, the modified starch can be added to the pulp furnish in an amount from about 0.5 to about 20 percent by weight, and preferably from about 3 to about 10 percent by weight based on the total weight of fibers.

- 20 The flow characteristics of a pulp furnish, including the furnish's ability to be dewatered, is an important factor in high speed papermaking methods and machines. One advantage of the invention is that the addition of modified starch to a pulp furnish does not adversely affect the furnish's flow characteristics despite the furnish's high retention of modified starch. Furthermore, the furnish is not adversely affected by the
25 addition of the modified starch when the pulp is treated with an anionic retention aid in accordance with the invention. The wet end addition of the modified starch to a pulp furnish treated with an anionic retention aid does not result in the formation of a gum-like precipitate, which would negatively impact the quality of the pulp furnish and limit its utility in high speed papermaking. Similarly, the addition of a cationic retention aid
30 to a pulp furnish containing an anionic retention aid and/or modified starch does not adversely affect the pulp furnish.

- The formation and properties of a representative paper product, OCC, containing modified starch is described in Example 4. The strength properties of the representative OCC product is summarized in Table 11. The results demonstrate that
35 the Mullen burst strength for an OCC product containing 3 percent by weight modified starch is increased by about 20% compared to a similarly constituted OCC product

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lacking modified starch. Increases in short span compression STFI, tensile, and stretch were also observed. The OCC product had an increase in short span compression STFI of about 5%, an increase in tensile of about 9%, and an increase in stretch of about 16% compared to a similarly constituted OCC product lacking modified starch.

5 Representative OCC products were also formed varying (a) the amount of cationic additive used to prepare the modified starch, (b) the amount of modified starch added to the pulp furnish, and (c) the type and amount of retention aid(s) added to the pulp furnish. The percentage starch retention results for various representative
10 OCC products is summarized in Table 12. Referring to Table 12, the results demonstrate that modified starch is highly retained by pulp and that modified starch retention can be increased through the use of retention aids. The anionic retention aid provided an enhancement in retention greater than the cationic retention aid.

EXAMPLES

Example 1

The Preparation of Representative Surface Charge Enhanced Starch

In this example, the preparation and physical properties of representative
starches having enhanced surface charge are described. The representative starches including a cationic polymer, a polyquaternary amine (PQA) were prepared as
20 described for Set 1. Representative starches including a polyquaternary amine and further including a retention aid (APAM) were prepared as described for Set 2.

Set 1. A cationic potato starch (Accosize 80, commercially available from Cytec Industries Inc., West Patterson, NJ) was cooked at 3.85% solids in a laboratory cooker (44 g, 86% solids) in 1000 mL of deionized water. A 0.1% solution of a
25 representative cationic polymer (a low molecular weight, highly positively charged polyquaternary amine, PQA, commercially available under the designation Nalco 7527 from Nalco Chemical Co., Naperville, IL) was diluted to 0.1% actives (1.43 g diluted to 500 mL).

In each of beakers 1, 2 and 3, 5.71 g of tapioca unmodified starch (5.0 g of
30 O.D.) was diluted to 50 mL with pH 10 buffer solution and allowed to sit for thirty minutes. In beaker 2, 0.95% cooked cationic potato starch was added (1.25 g of 3.78% solution) and mixed well. In beaker 3, 5 lb/ton Nalco 7527 was added (12.5 g of 0.1% solution) and mixed well. All three beakers equilibrated for thirty minutes prior to microscopic observation.

35 All three beakers were then adjusted to pH 7 with 1 N sulfuric acid and observed using a microscope. Ten percent by weight (O.D. pulp basis) of the three

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starch samples (1 mL of starch at about 7% solids) was added each to 1.0 g O.D. pulp (hardwood bleached kraft pulp, HWBK, Aspen, disintegrated, commercially available from Weyerhaeuser Co.) at a 0.5% consistency and mixed. The starch samples were microscopically observed.

- 5 Set 2. Cationic potato starch (Accosize 80), was cooked at 4.5% solids in a laboratory cooker (69 g, at 86% solids in 1340 mL of deionized water). A 0.1% solution of Nalco 7527 was diluted to 0.1% actives (1.43 g diluted to 500 mL). A 0.1% solution of a representative retention aid (a high molecular weight, slightly negatively charged polyacrylamide, APAM, commercially available under the
10 designation Accurac 171 from Cytec Industries Inc., West Patterson, NJ) was diluted to 0.01% actives (1.43 g diluted to 500 mL and diluted 10 times):

- In each of beakers 1, 2 and 3, 5.0 g of tapioca unmodified starch (4.4 g of O.D.) was diluted to 50 mL, with pH 10 buffer solution and allowed to equilibrate for fifteen minutes. In beaker 2, 1.3% cationic potato starch (Accosize 80) was added
15 (1.25 g of 4.5% solution) and mixed well. In beaker 3, 5.7 lb/ton PQA (Nalco 7527) was added (12.5 g of 0.1% solution) and mixed well. After the chemical additions, the solutions were equilibrated for thirty minutes. All three beakers were then adjusted to pH 7 with 1 N sulfuric acid and allowed to stand for one hour.

- Pulp treatment. Hardwood bleached kraft pulp (HWBK) was disintegrated and
20 diluted to 0.25% consistency with deionized water. To each of six beakers, 0.5 g pulp at 0.25% consistency was added. Three of the pulp samples were pretreated with APAM by adding 0.5 lb/ton (1.25 g of 0.01% solution). The pulp was well mixed and then starch solutions were added to the pulp samples. To the pulp samples that were not pretreated, 0.5 lb/ton APAM (1.25 g of 0.01% solution) was then added and
25 mixed. All six conditions were qualitatively analyzed using a microscope.

- The first experiment was designed to qualitatively compare unmodified tapioca starch with the addition of cooked cationic potato starch or a cationic polymer, polyquaternary amine (PQA). A microscope was used to observe any physical changes or reactions with other starch particles or fibers. The microscope observations are
30 summarized in Table 1.

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Table 1. Qualitative microscopic observations.

Beaker	After Chemical Addition	After pH Adjustment	Reaction with Fibers
1 (Control)	No flocculation	No flocculation	No interaction
2 (Cationic starch)	Some flocculation	Some flocculation	Some interaction
3 (PQA)	No flocculation	No flocculation (Highly dispersed)	Some interaction

After the addition of the PQA and reduction of the pH, there was a noticeable difference in the behavior of the starch slurry. The starch granules appeared highly dispersed. There was also some interaction between the modified starch and the fibers before and after the pH adjustment. The addition of both cooked starch and PQA caused the starch particles to have some interaction when added to fiber.

The effect of post- or pretreating fibers with an anionic polymer (APAM) on the reaction of the modified starch solutions was also determined. In one case, APAM was added to the fiber before addition of the starch slurry, and in the second case, APAM was added after the addition of the starch to the fibers. The observations are summarized in Table 2.

Table 2. Qualitative microscopic observations.

Beaker	Fibers Pretreated with APAM	Fibers Post-Treated with APAM
1 (Control)	No fiber interaction	Starch particles lying uniformly on fiber
2 (Cationic starch)	Some starch agglomeration/fiber interaction	Some starch agglomeration/fiber interaction
3 (PQA)	No fiber interaction	No fiber interaction

Treatment with APAM had an insignificant effect on the appearance of fibers treated with either the cationic starch and PQA-modified starch.

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Example 2The Measurement of Surface Charge of Representative Surface Charge Enhanced Starch Particles

5 In this example, the measurement of the surface charge of representative starch particles having enhanced surface charge are described. The surface charge was determined by zeta potential measurement.

Sets 1 and 2: Control and Modified Starches. Unmodified tapioca starch was used for each test. To each starch sample (5.0 g) was added 50 mL pH 10 buffer solution and the solution was allowed to stand for one hour. After standing for one hour, 5 lb/ton (actives basis) PQA (Nalco 7527) was added to the starch and mixed well to provide the "modified sample". In the control sample, no polymer was added. The samples were allowed to stand for an additional hour before adjusting to pH 7 with 1 N sulfuric acid. The samples were allowed to stand for an additional hour prior to analysis.

15 Set 3: Modified Starches from pH Variance. The modified sample was prepared by adding 5.0 g of unmodified tapioca starch in 50 mL of pH 10 buffer (as described above) and allowed to stand for one hour before adding 5 lb/ton PQA (Nalco 7527). After one hour, the pH was adjusted to pH 7 with 1 N sulfuric acid and allowed to stand for one final hour. A second sample was prepared by adding pH 10

20 buffer to 5.0 g of tapioca starch as received and then allowed to stand. After the hour, 5 lb/ton PQA (Nalco 7527) was added and was allowed to stand for another two hours with no further pH adjustment. A third sample was prepared as described above except that pH 7 buffer was added to the starch with no further pH adjustment.

Zeta Potential Measurement. The zeta potentials for all samples were

25 measured using a Delsa 440 (Coulter Electronics, Inc., Hialeah, FL) run at a frequency range of ± 500 Hz, and with a current equal to one-half the value of the conductivity of the sample. The sample was run at two cell heights (16 and 84). Due to the addition of the PQA, the samples stayed fairly well dispersed and were allowed to settle for one hour prior to analysis.

30 The zeta potential results from the Set 1 samples are shown in Table 3. The charge is an average at 8.6, 17.1, 25.6, and 34.2° angles at both the 16 and 84 cell heights. The control (unmodified sample) was run in triplicate and the modified sample was run in duplicate. The results demonstrate that the addition of the cationic polyacrylamide gave the modified sample a significantly enhanced charge compared to

35 the control.

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Table 3. Starch zeta potential measurement results.

Sample	PQA (lb/ton)	pH	Conductivity (ms/cm)	Average (mV)
Control	0	7	6.1	1.59
Control	0	7	9.5	2.67
Control	0	7	9.8	-2.95
Modified	5	7	7.7	17.35
Modified	5	7	9.1	18.22

The zeta potential results from the Set 2 samples are shown in Table 4. Because settling in a zeta potential cell can shift the stationary plane, an experiment was conducted testing samples of various consistency to determine the effect on the charge analysis. The consistencies were varied by varying settling times of the starch slurries prior to analysis. The same samples were prepared as with the first set, and included a control and a modified sample. The modified sample was also washed with deionized water to determine whether the charge was on the particle surface or merely weakly associated with the surface.

Table 4. Starch zeta potential measurement results.

Starch	PQA (lb/ton)	pH	Condition	Conductivity (ms/cm)	Settling Time (min)	Average (mV)
Control	0	7	Unwashed	6.96	0	-2.08
Control	0	7	Unwashed	9.75	9	-2.19
Control	0	7	Unwashed	9.82	15	-2.47
Modified	5	7	Unwashed	6.86	0	10.72
Modified	5	7	Unwashed	7.95	9	15.24
Modified	5	7	Washed	8.40	9	10.10

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The results show that settling time does effect the zeta potential measurement. The results further indicate that the charge is on the particle surface and not merely weakly associated with the surface, and that washing the starch particles has an insignificant effect on zeta potential measurement.

- 5 To determine the effect of pH on modified starch formation and on the overall particle charge, three samples (Set 3 samples prepared as described above) were compared. The results are shown in Table 5.

Table 5. Effect of pH adjustment on charge.

Starch	7527 (lb/ton)	Initial pH	Final pH	Conductivity (ms/cm)	Settling Time (min.)	Average (mv)
Modified	5	7	7	6.79	60	17.25
Modified	5	10	10	8.00	60	15.86
Modified	5	10	7	8.05	60	18.29

- 10 All of the modified samples had a similar cationic charge. It does not appear that the pH adjustment had a significant effect on the modification process surface charge.

Example 3

15 Pulp Retention of Representative Surface Charge Enhanced Starch

In this example, the retention of representative starch having enhanced surface charge by pulp is described. To determine whether the modified starch can be retained in high shear conditions, a Britt Jar was used for retention studies.

- 20 Pulp Preparation. Prince Albert hardwood was refined to a 400 mL CSF with the Escher Wyss conical refiner (Bird Escher Wyss, Manfield, MA) using the following conditions: 3.0% consistency, 1.0 W-s/m specific edge load, 1250 rpm, 0.583 km/s cutting length, and 60 degree bar angle. Prince Albert softwood was also refined to a 600 mL CSF with the Escher Wyss using the same conditions except that the specific edge load was 3.0 W-s/m. The net power specific energy for the hardwood was 48.6
- 25 kW-h/t and for the softwood was 1.75 kW-h/t. A pulp blend of 60% hardwood and 40% softwood was prepared. The fines were removed using a 200 mesh screen box. The final freeness value of the pulp mixture without fines was 695 mL at a 2.2% consistency.

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Britt Jar Conditions. A Britt Jar having a 100 mesh conical mesh screen was used in the retention determination. The pulp was added into a vaned Britt Jar with the stopper close and mixed with the starch at various speeds. After time had elapsed for sampling, the stopper was opened and the filtrate was collected in a tared aluminum pan (around 100 mL). The pan was immediately weighed on the same four-place balance that was used for the tare. The pan was put into a 105°C oven until the following day. The dried sample was placed into a desiccator before reweighing the pan. The consistency of the unretained slurry was calculated from Equation 1.

$$\text{Filtrate Consistency} = \frac{\text{O.D. grams residue}}{\text{Total Grams Filtrate}} \quad (1)$$

10 The percent retained from the pulp slurry was calculated using Equation 2.

$$\text{Percent Retained} = \frac{\text{Pulp Slurry Consistency} - \text{Filtrate Consistency}}{\text{Pulp Slurry Consistency}} \times 100 \quad (2)$$

15 To determine the correct degree of shear or mixing speed, an initial study was done with a typical alkaline fine paper furnish. The retention of starch formed in accordance with the present invention was compared to the retention of precipitated calcium carbonate.

Chemicals. The pulp prepared as described above was diluted to 0.65% consistency with deionized water. Precipitated calcium carbonate (PCC) was obtained from Specialty Minerals, Inc., Bethlehem, PA and had 31.6% solids. A highly charged, high molecular weight anionic polyacrylamide (APAM, Accurac 171) solution was prepared by diluting 1.43 g APAM to 500 mL with deionized water. The solution was mixed with a Braun hand blender for fifteen seconds to provide a 0.1% APAM solution and then diluted 10X by diluting 50 mL of 0.1% to 500 mL with deionized water to provide a 0.01% solution. A cationic potato starch (Accosize 80) solution was prepared by mixing 69.9 g of starch (86% solids) with 1340 mL of deionized water at 4.5% solid.

Britt Jar Procedure. Pulp (2.5 g, 385 g of 0.65% consistency) was added to the Britt Jar. Table 6 shows the chemical additions and the amounts made to the pulp samples with the mixing times following each addition.

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Table 6. Chemical order of addition and mixing times.

Chemical	Mixing Time (seconds)
17 lb/ton cationic starch (0.47 g of 4.5%)	15
20% PCC (1.58 g of 31.6%)	15
0.5 lb/ton APAM (6.25 g of 0.01%)	30

The above conditions were run at three different mixing speeds, 500, 100, and 1500 rpm, with the ultimate goal of obtaining realistic filler retention. Typical filler retention on a fine paper machine is between 50-55% retention. Table 7 provides the mixing speed results.

Table 7. Britt Jar filler retention: Mixing speed variance.

Mixing speed (rpm)	Percent filler retention
500	50.4
1000	8.95
1500	4.5

Referring to Table 7, the 500 rpm data set provides effective retention while the higher mixing speed conditions show inadequate retention.

Modified Starch Retention

The retention of the modified starch of the present invention was compared to a typical alkaline fine paper furnish with PCC. The APAM and cationic starch solutions were prepared the same as described above. In addition, a PQA solution (Nalco 7527) was prepared by diluting 1.43 g stock to 500 mL with deionized water. The PQA solution was 0.1% actives and was mixed for fifteen seconds with a Braun hand blender. PCC was as described above. The pulp was diluted to 0.42% consistency with deionized water.

The modified starch was prepared by diluting 5.0 g (12.5% solids) of unmodified tapioca starch to 50 mL with pH 10 buffer solution. The starch was well mixed and allowed to stand for one hour. A volume of 12.5 mL of 0.1% PQA (Nalco 7527) was added and mixed well. The solution was allowed to stand for another hour. The pH was then adjusted to pH 7 with 1 N sulfuric acid (about 2.7 mL). The final consistency of the starch solution was 6.7%.

The control starch was prepared by diluting 5.0 g (12.5% solids) of unmodified tapioca starch to 50 mL with pH 10 buffer solution. The starch was mixed well and

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was allowed to stand for one hour. A volume of 12.5 mL of deionized water was added and mixed well. The solution was allowed to stand for another hour. The pH was then adjusted to pH 7 with 1 N sulfuric acid (about 2.7 mL). The final consistency of the starch solution was 6.7%.

- 5 **Britt Jar Procedure.** For each Britt Jar experiment, 2.5 g pulp (595 g at 0.42% consistency) was added and mixed using 500 rpm. For the control starch and the modified starch, 6.5 g of 6.7% starch was added (17.4%). For the APAM, 6.25 mL of a 0.01% solution was added (0.5 lb/ton) and for the cationic potato starch, 0.5 g of 4.5% solids was added (17 lb/ton). For the PCC, 1.6 g of 31.6% solution was added
- 10 (20%). The conditions are summarized in Table 8. Each condition was run in triplicate and the entire experiment was randomized (except for the alkaline fine paper furnish which was completed first in triplicate.)

Table 8. Britt Jar chemical conditions.

First Addition	Mixing Time (s)	Second Addition	Mixing Time (s)
17.4% Modified Starch	30	None	30
17.4% Modified Starch	30	0.5 lb/ton APAM	30
0.5 lb/ton APAM	30	17.4% Modified Starch	30
17.4% Control Starch	30	None	30
17.4% Control Starch	30	0.5 lb/ton APAM	30
0.5 lb/ton APAM	30	17.4% Control Starch	30
17 lb/ton Cationic Starch/ 20% PCC	15/15	0.5 lb/ton APAM	30

The filler (modified starch or PCC) retentions are summarized in Table 9.

Table 9. Britt Jar filler retention: Order of addition variance.

Sample (First/Second Addition)	Percent filler retention
Control/APAM	5
Modified/APAM	58
Cationic starch/PCC/APAM	45
APAM/Control	3
APAM/Modified	72
Control/None	1
Modified/None	10

The highest retention was achieved with the addition of the APAM to the pulp followed by the addition of the modified starch. The second highest retention was the addition of the modified starch to the pulp followed by the APAM addition. Both of these conditions had a higher filler retention than the typical alkaline fine paper system.

Effect of Treatment pH on Modified Starch Retention

Pulp having the greatest starch retention was obtained using pulp fibers that had been pretreated with APAM. To evaluate the effect of pH on the modified starch retention by pulp, pulp was treated with the modified starch under three different pH conditions. The pulp, APAM, and PQA solutions were prepared as described above. The original pulp mixture was diluted to 0.41% consistency with deionized water. To add 2.5 g of O.D. pulp, 605 g of the 0.41% solution was used for each condition. Three starch solutions were prepared as follows.

Modified Starch pH 10-7. Five grams (12.5% solids) of unmodified tapioca starch was diluted to 50 mL with pH 10 buffer solution. The starch was mixed well and was allowed to stand for one hour. A volume of 12.5 mL of 0.1% Nalco 7527 was added and mixed well. The solution was allowed to stand for another hour. The pH was then adjusted to pH 7 with 1 N sulfuric acid (about 2.7 mL). The solutions equilibrated for one more hour. The final consistency of the starch solution was 6.7%.

Modified Starch pH 10-10. Five grams (12.5% solids) of unmodified tapioca starch was diluted to 50 mL with pH 10 buffer solution. The starch was mixed well and was allowed to stand for one hour. A volume of 12.5 mL of 0.1% Nalco 7527 was added and mixed well. The solution was allowed to stand for two hours. The final consistency of the starch solution was 6.7%.

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Modified Starch pH 7- 7. Five grams (12.5% solids) of unmodified tapioca starch was diluted to 50 mL with pH 7 buffer solution. The starch was mixed well and was allowed to stand for one hour. 12.5 mL of 0.1% Nalco 7527 was added and mixed well. The solution was allowed to stand for two hours. The final consistency of the starch solution was 6.7%.

Britt Jar Procedure. APAM was added to the pulp in the Britt Jar followed by mixing for 30 seconds followed by the addition of the starch slurry. For each run, 0.5 lb/ton APAM (6.25 mL 0.01% solution) and 20% starch (7.4 mL of a 6.74% solution) were added. The experiment was randomized and each condition was run in triplicate. The results of pH variance are summarized in Table 10.

Table 10. Britt jar filler retention: pH variance.

APAM/Modified	Percent filler retention
pH10/pH10	69
pH10/pH7	75
pH7/pH7	77

All of the tested conditions show a high retention of starch with the pH 7/pH 7 method providing slightly greater retention than the pH 10/pH 10 condition.

Example 4

The Formation and Properties of OCC Containing Representative Surface Charge Enhanced Starch

In this example, the formation and properties of old corrugated cardboard (OCC) containing modified starch is described. The properties of representative OCC products was determined and compared to OCC products that did not include modified starch.

The OCC product was formed from a fibrous furnish containing 100 percent OCC. Modified starch was prepared as described above by adding 5 lb PQA (Nalco 7527)/ton starch. The pulp furnish was treated with 0.5 lb APAM (Accurac 171)/ton fiber followed by the addition of 3 percent by weight modified starch based on the total weight of fiber, and then 5 lb CPAM (Accurac 182RS)/ton fiber. After depositing the pulp furnish containing the modified starch onto a foraminous support, the deposited pulp was dewatered, and then dried to provide the OCC product.

The properties of the OCC product prepared as described above are summarized in Table 11. In the table, Sample 1 refers to an OCC product that was formed without the inclusion of modified starch and Sample 2 refers to an OCC

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product that includes 3 percent by weight modified starch based on the total weight of fiber. In the table, SSC STFI and TEA refer to short span compression STFI and tensile energy adsorption, respectively.

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Table 11. Properties of OCC containing modified starch.

Sample #	Basis Wt lb/Msf	Caliper points	Density kg/m ³	Burst (Mullen) lbs	Index	SSC STFI lbs/in	Index	Tensile lbs/in	Index	Stretch %	TEA inlb/in ²
1	32.7	13.3	473.9	54	45.9	12.35	11.3	21.9	20.1	2.746	0.4379
2	32.2	12.9	481.1	64	59.6	12.8	11.9	24.6	22.9	3.191	0.5657

Referring to Table 11, the Mullen burst strength for OCC product Samples 1 and 2 represent an increase of about 20% compared to similarly constituted OCC lacking modified starch. Increases in short span compression STFI, tensile, and stretch were also observed. The OCC product containing modified starch had an increase in short span compression STFI of about 5%, an increase in tensile of about 9%, and an increase in stretch of about 16% compared to a similarly constituted OCC product lacking modified starch.

The weight percentage of starch retained in representative OCC products were compared to each other and compared to OCC products containing unmodified starch. The results are summarized in Tables 12-15.

Several representative OCC products were formed varying the amount of cationic additive used to prepare the modified starch, the amount of modified starch added to the pulp furnish, and the type and amount of retention aid(s) added to the pulp furnish. The percentage starch retention results for various representative OCC products is summarized in Table 12. In these products, the cationic additive used in forming the modified starch was PQA (Nalco 7527), the anionic retention aid was APAM (Accurac 171), and the cationic retention aid was CPAM (Accurac 182). The following terms are used in Table 12:

Modified Starch refers to starch modified with 5 lb PQA (Nalco 7527)/ton starch;

Variable PQA refers to an OCC product prepared by pretreating the pulp furnish with 0.5 lb APAM (Accurac 171)/ton fiber prior to treatment with modified starch prepared from starch and variable amounts of PQA (Nalco 7527): A, B, C, and D refer to OCC products containing modified starch prepared from 1, 2, 3, 5, and 7 lb PQA (Nalco 7527)/ton starch;

Variable APAM refers to an OCC product prepared by pretreating the pulp furnish with variable amounts of APAM (Accurac 171) followed by treatment with modified starch prepared from starch and 5 lb PQA (Nalco 7527)/ton starch: E, F, and G refer to OCC products in which the pulp furnish was pretreated with 0.25, 0.50, and 0.75 lb APAM (Accurac 171)/ton fiber;

APAM/PQA/APAM refers to an OCC product in which the pulp furnish was pretreated with 0.25 lb APAM (Accurac 171), and then treated with modified starch prepared from starch and 5 lb PQA (Nalco 7527)/ton starch and 0.25 lb APAM (Accurac 171)/ton fiber;

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APAM/PQA/CPAM refers to an OCC product in which the pulp furnish was pretreated with 0.25 lb APAM (Accurac 171), then treated with modified starch prepared from starch and 5 lb PQA (Nalco 7527)/ton starch followed by 2.0 lb CPAM (Accurac 182)/ton fiber; and

- 5 Variable CPAM refers to an OCC product prepared by treating the pulp furnish with variable amounts of CPAM (Accurac 182) after treatment with modified starch prepared from starch and 5 lb PQA (Nalco 7527)/ton starch: H, I, and J refer to OCC products in which the pulp furnish was treated with 1.0, 2.0, and 3.0 lb CPAM (Accurac 182)/ton fiber;

10 Table 12. OCC starch retention comparison.

OCC Filler	Percent Retention
Starch	1.45
Modified starch	20.82
Variable PQA	
A	79.19
B	95.63
C	94.52
D	88.20
Variable APAM	
E	82.83
F	94.52
G	88.65
APAM/PQA/APAM	81.29
APAM/PQA/CPAM	76.45
Variable CPAM	
H	37.50
I	42.31
J	45.42

The results in Table 12 demonstrate that modified starch is highly retained by pulp and that modified starch retention can be increased through the use of retention aids. The anionic retention aid provided an enhancement in retention greater than the cationic retention aid.

- 15 The weight percentage of modified starch retained in representative OCC products as a function of the amount of starch cationic additive (PQA, Nalco

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7527)/ton starch, with pretreatment with 0.5 lb anionic retention aid (APAM, Accurac 171)/ton fiber was determined. The results are summarized in Table 13.

Table 13. OCC starch retention: PQA variance.

PQA (lb/ton)	Percent Retention
1	84.5
1	73.9
3	87.7
3	103.6
5	94.5
5	94.6
7	88.8
7	87.6

- 5 The results demonstrate that significant retention was achieved using from 1 to 7 lb PQA/ton starch, with about 5 lb PQA/ton starch providing near optimum retention.

 The weight percentage of modified starch (5 lb PQA/ton starch) retained in representative OCC products as a function of pretreatment with varying amounts of anionic retention aid (APAM, Accurac 171) was determined. The results are summarized in Table 14.

Table 14. OCC starch retention: APAM variance.

APAM (lb/ton)	Percent Retention
0.25	79.5
0.25	86.1
0.50	94.5
0.50	94.6
0.75	89.0
0.75	88.3

- 15 The results demonstrate that optimum retention was achieved for pretreatment with 0.50 lb anionic retention aid/ton fiber.

 The weight percentage of modified starch (5 lb PQA/ton starch) retained in representative OCC products as a function of treatment with varying amounts of

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cationic retention aid (CPAM, Accurac 182) was determined. The results are summarized in Table 14.

Table 15. OCC starch retention: CPAM variance.

CPAM (lb/ton)	Percent Retention
1	27.1
1	47.9
2	42.5
2	42.2
3	44.4
3	46.5

- 5 The results demonstrate that significant retention was achieved using from 1 to 3 lb CPAM/ton starch.

While the preferred embodiment of the invention has been illustrated and described, it will be appreciated that various changes can be made therein without departing from the spirit and scope of the invention.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A composition comprising a polysaccharide particle and a cationic additive, wherein the cationic additive is adhered to the polysaccharide particle to provide a polysaccharide particle having a positive surface charge.
2. The composition of Claim 1 wherein the cationic additive comprises a cationic polymer.
3. The composition of Claim 2 wherein the cationic polymer comprises a polyquaternary amine.
4. The composition of Claim 3 wherein the polyquaternary amine has a molecular weight in the range from about 1 million to about 5 million grams per mole.
5. The composition of Claim 3 wherein the polyquaternary amine has about 3 meq quaternary amine per gram.
6. The composition of Claim 1 wherein the cationic additive is present in the composition in an amount from about 1 to about 15 pounds per ton polysaccharide.
7. The composition of Claim 1 wherein the surface charge is in the range from about +1 mV to about +100 mV.
8. The composition of Claim 1 wherein the polysaccharide is selected from the group consisting of corn, potato, tapioca, pea, and wheat starches.
9. A pulp furnish comprising a polysaccharide particle having a positive surface charge, wherein the polysaccharide particle having a positive surface charge comprises a cationic additive adhered to the polysaccharide particle.
10. The furnish of Claim 9 wherein the cationic additive comprises a cationic polymer.
11. The furnish of Claim 10 wherein the cationic polymer comprises a polyquaternary amine.

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12. The furnish of Claim 9 wherein the polysaccharide particle has a surface charge in the range from about +1 mV to about +100 mV.
13. The furnish of Claim 9 further comprising an anionic retention aid.
14. The furnish of Claim 9 further comprising a cationic retention aid.
- 5 15. The furnish of Claim 13 further comprising a cationic retention aid.
16. The furnish of Claim 13 wherein the anionic retention aid comprises an anionic polyacrylamide.
17. The furnish of Claim 16 wherein the anionic polyacrylamide comprises a copolymer of acrylic acid and acrylamide.
- 10 18. The furnish of Claim 17 wherein the copolymer comprises about 30 mole percent acrylic acid and about 70 mole percent acrylamide.
19. The furnish of Claim 17 wherein the copolymer has a molecular weight in the range from about 8 to about 15 million grams per mole.
20. The furnish of Claim 13 wherein the anionic retention aid is present in
15 the furnish in an amount from about 0.1 to about 3.0 pounds per ton fiber.
21. The furnish of Claim 14 wherein the cationic retention aid comprises a cationic polyacrylamide.
22. The furnish of Claim 21 wherein the cationic polyacrylamide comprises a copolymer of acrylamide and a quaternary amine monomer.
- 20 23. The furnish of Claim 22 wherein the copolymer comprises about 90 mole percent acrylamide and about 10 mole percent quaternary amine monomer.
24. The furnish of Claim 22 wherein the copolymer has a molecular weight in the range from about 8 to about 15 million grams per mole.
25. The furnish of Claim 14 wherein the cationic retention aid is present in
25 the furnish in an amount from about 0.1 to about 12 pounds per ton fiber.

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26. A paper product comprising a polysaccharide particle having a positive surface charge, wherein the polysaccharide particle having a positive surface charge comprises a cationic additive adhered to the polysaccharide particle.

27. The paper product of Claim 26 wherein the cationic additive comprises
5 a cationic polymer.

28. The paper product of Claim 27 wherein the cationic polymer comprises a polyquaternary amine.

29. The paper product of Claim 26 wherein the polysaccharide particle has a surface charge in the range from about +1 mV to about +100 mV.

10 30. The paper product of Claim 26 further comprising an anionic retention aid.

31. The paper product of Claim 26 further comprising a cationic retention aid.

15 32. The paper product of Claim 30 further comprising a cationic retention aid.

33. The paper product of Claim 30 wherein the anionic retention aid comprises an anionic polyacrylamide.

34. The paper product of Claim 31 wherein the cationic retention aid comprises a cationic polyacrylamide.

20 35. The paper product of Claim 26 wherein the paper product is selected from the group consisting of fine paper, newsprint, bleached board, liner board, medium board, and old corrugated cardboard.

36. A method for forming a paper product comprising:
adding a polysaccharide particle having a positive surface charge to a first pulp
25 furnish to provide a second pulp furnish, wherein the polysaccharide particle having a positive surface charge comprises a cationic additive adhered to the polysaccharide particle;

depositing the second pulp furnish onto a foraminous support to provide a wet web; and

30 dewatering and drying the wet web to provide the paper product.

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37. The method of Claim 36 wherein the cationic additive comprises a cationic polymer.

38. The method of Claim 37 wherein the cationic polymer comprises a polyquaternary amine.

5 39. The method of Claim 36 wherein the starch particle has a surface charge in the range from about +1 mV to about +100 mV.

40. The method of Claim 36 further comprising adding an anionic retention aid to the first pulp furnish.

10 41. The method of Claim 36 further comprising adding a cationic retention aid to the first pulp furnish.

42. The method of Claim 40 further comprising adding a cationic retention aid to the first pulp furnish.

43. The method of Claim 40 wherein the anionic retention aid comprises an anionic polyacrylamide.

15 44. The method of Claim 41 wherein the cationic retention aid comprises a cationic polyacrylamide.

45. The method of Claim 36 wherein the paper product is selected from the group consisting of fine paper, newsprint, bleached board, liner board, medium board, and old corrugated cardboard.

20 46. A method for increasing the strength of a paper product comprising:
adding a polysaccharide particle having a positive surface charge to a first pulp furnish to provide a second pulp furnish, wherein the polysaccharide particle having a positive surface charge comprises a cationic additive adhered to the polysaccharide particle;

25 depositing the second pulp furnish onto a foraminous support to provide a wet web; and

dewatering and drying the wet web to provide the paper product having increased strength compared to a similarly constituted paper lacking a polysaccharide particle having a positive surface charge.

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47. The method of Claim 46 wherein the cationic additive comprises a cationic polymer.

48. The method of Claim 47 wherein the cationic polymer comprises a polyquaternary amine.

5 49. The method of Claim 47 wherein the polysaccharide particle has a surface charge in the range from about +1 mV to about +100 mV.

50. The method of Claim 47 further comprising adding an anionic retention aid to the first pulp furnish.

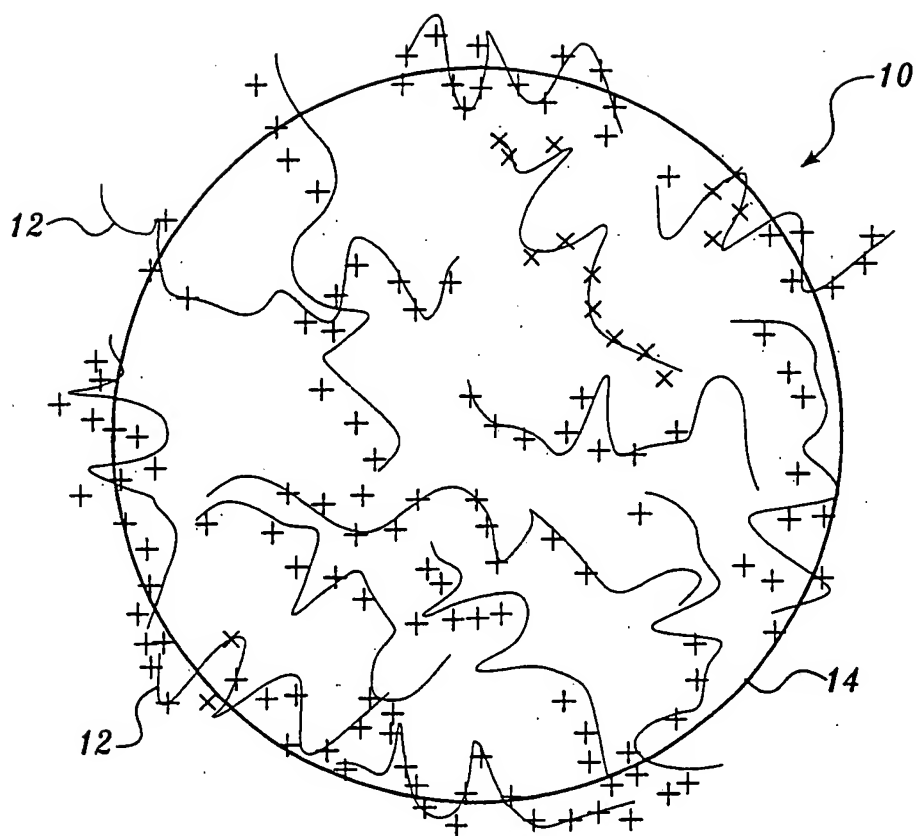
10 51. The method of Claim 47 further comprising adding a cationic retention aid to the first pulp furnish.

52. The method of Claim 50 further comprising adding a cationic retention aid to the first pulp furnish.

53. The method of Claim 50 wherein the anionic retention aid comprises an anionic polyacrylamide.

15 54. The method of Claim 52 wherein the cationic retention aid comprises a cationic polyacrylamide.

55. The method of Claim 46 wherein the paper product is selected from the group consisting of fine paper, newsprint, bleached board, liner board, medium board, and old corrugated cardboard.

*Fig. 1.*

INTERNATIONAL SEARCH REPORT

Inter. nal Application No

PCT/US 00/24561

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D21H17/29

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No

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